

Biodegradation of starch/polylactic acid/poly(hydroxyester-ether) composite bars in soil[☆]

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Received 18 July 2002; received in revised form 5 November 2002; accepted 9 November 2002

Abstract

Injection molded tensile bars composed of native corn starch (0–70%), poly(D,L-lactic acid) (95% L) (PLA, 13–100%) and poly(hydroxyester-ether) (PHEE, 0–27%) were buried in soil for 1 year in order to study the effects of starch and PHEE on rates of biodegradation. Rates of weight loss increased in the order pure PLA (~0%/year) < starch/PLA (0–15%/year) < starch/PHEE/PLA (4–50%/year) and increased with increasing starch and PHEE contents. Weight losses were due to starch only with the degradation proceeding from outside to inside along a narrow zone. Tensile strength did not change with time for pure PLA and, after an initial decline, did not change much for the other compositions. Some formulations containing PHEE and lower (40%) starch levels had higher tensile strengths after initial exposure to soil than those without PHEE.

Published by Elsevier Science Ltd.

Keywords: Starch; Poly(lactic acid); Epoxy; Biodegradable

1. Introduction

Poly(lactic acid) (PLA) is a degradable thermoplastic polymer with excellent mechanical properties which is beginning to be produced on a large scale from fermentation of corn to lactic acid and subsequent chemical polymerization [1–3]. Poly(hydroxyester-ethers) (PHEE) are thermoplastic epoxy resins which are compostable [4,5]. Our research has focused on composites of PLA with starch to reduce cost and modify degradation rates and with PHEE to improve compatibility and processibility [6]. Previous studies have shown that starch/PLA composites have rather poor mechanical properties due to poor adhesion of starch and PLA [7,8]. In contrast, work at the National Center for Agricultural Utilization Research (NCAUR) has shown that starch/PHEE composites show good interfacial adhesion and

mechanical properties [9,10]. Recent work has shown that addition of PHEE to starch/PLA composites improves adhesion and also lowers pressures needed for injection molding [6]. Both durable and disposable applications are envisioned for these resins and composites thereof and hence it would be of interest to determine their degradability in different natural environments.

Most studies of the degradation of PLA have focused on abiotic hydrolysis due to the long standing use of PLA as biomedical implants [3]. Degradation occurs in stages, the first being diffusion of water into the material, hydrolysis of ester bonds and lowering of molecular weight followed by intracellular uptake of lactic acid oligomers and catabolism. Rates of hydrolysis increase with water content and temperature [3,11] and are catalyzed by free carboxyl groups of the hydrolyzed PLA ends. Li et al. [12] found that hydrolysis is actually faster in the interior of a thick sample since carboxylic acid concentration was higher there than the exterior due to leaching of the acidic PLA oligomers into the surrounding aqueous medium.

Several studies have shown that certain proteases, including proteinase K, pronase and bromelain have been found to increase the rate of degradation of PLA

[☆] Product names are necessary to report factually on available data; however the USDA neither guarantees nor warrants the standard of the product, and the use of the name USDA implies no approval of the product to the exclusion of others that may also be suitable.

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while esterases do not [3,13]. Pranamuda et al. [14] found that PLA degrading organisms are sparsely distributed in soil environments and found only one, an actinomycete *Amycolatopsis* sp. that degraded PLA in culture at 30 °C. Jarerat and Tokiwa [15] showed that PLA was degraded by the fungus *Tritirachium album* at 30 °C only if gelatin was added to the medium. Hakkarainen et al. [16] found that PLA films were degraded to a powder after 5 weeks in a mixed culture of compost microorganisms at 30 °C whereas the film in the abiotic medium looked intact. They also found PLA molecular weights, especially Mn were reduced to a greater extent in the biotic medium, probably due to cleavage near the chain ends. Other authors claim that initial degradation is due to abiotic hydrolysis only followed by biotic assimilation of breakdown products [3,17]. PLA is completely mineralized to CO₂, water and a small amount of biomass after 4–6 weeks in compost (~60 °C) [1,2,18,19].

There have been relatively few reports of the biodegradability of PLA in soil and how addition of fillers and other polymers might affect degradation rates. Torres et al. [20] found growth of fungal mycelia on racemic PLA plates after 8 weeks in soil. Urayama et al. [21] found only a 20% decrease in molecular weight of PLA (100% L) plates after 20 months in soil while a 75% decrease was noted for PLA (70% L). Ho and Pometto [22] found that about 20% of a PLA film was mineralized to CO₂ after 182 days in a laboratory

respirometer charged with soil at 28 °C. Calmon et al. [23] found that PLA films had weight losses varying from 0 to 100% after burial in soil for 2 years depending on PLA type and location. Osawa et al. [24] found that the molecular weight of PLA in PLA/starch 70/30 moldings decreased by about 60% after burial in soil for 45 days versus 10% for PLA alone. Acceleration of PLA degradation in blends with polyethylene glycol [25] and cellulose [26] was claimed. In this study, we have examined the effects of different starch and PHEE levels on the rates of weight loss and tensile strength of injection molded PLA bars in soil over 1 year.

2. Experimental

2.1. Materials

Granular (native) corn starch was Buffalo 3401 from CPC International, Englewood Cliffs, NJ. It was dried in a forced air oven at 105 °C for 4 days to <1% moisture. PLA was from Cargill Dow Polymers, Minnetonka, MN, was 95% L and had an M_w of 324,000. PHEE was from Dow Chemical, Midland, MI, was a reaction product of bis-phenol-A diglycidylether and adipic acid [4] and had an M_w of 58,000. Wax OP (mold release agent) was obtained from Clariant, Charlotte, NC and was added to the starch to give an overall level of 1%.

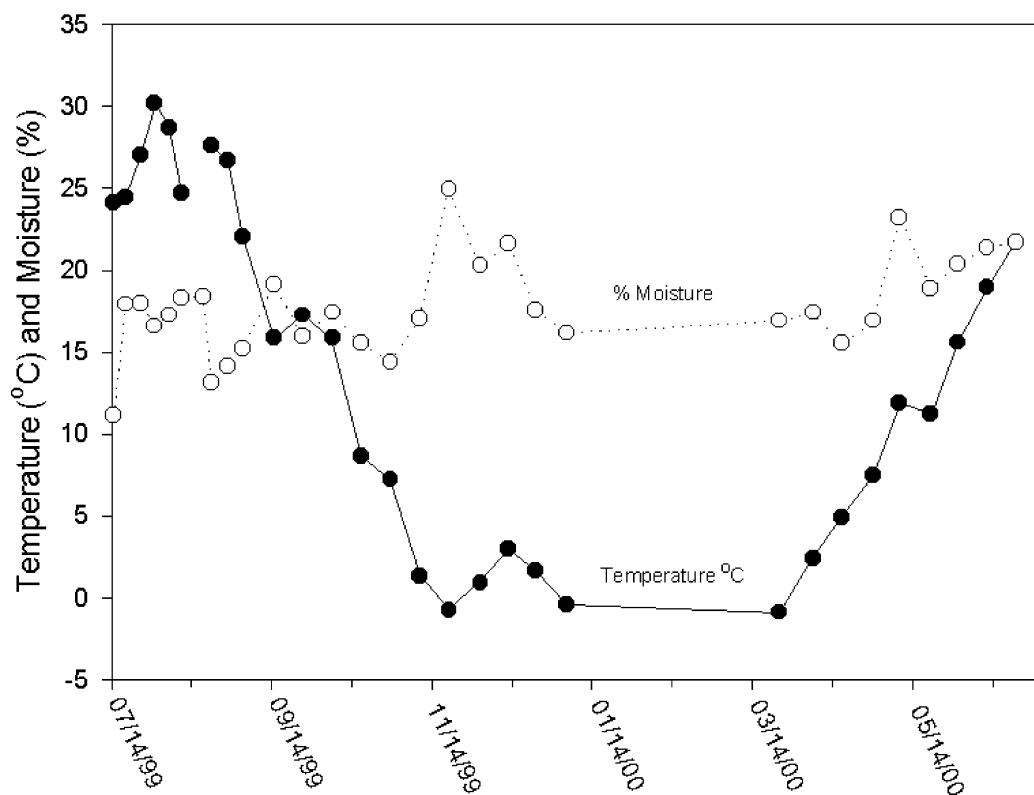


Fig. 1. History of soil temperatures (●) and moistures (○) during burial study.

2.2. Methods

Formulations were compounded on a Werner Pfleiderer ZSK-30 42/1 twin screw extruder (Ramsey, NJ) as described previously [6]. Barrel and die temperatures were 52–182 and 80 °C, respectively. PLA and PHEE were introduced into barrel section one using a calibrated AccuRate (Whitewater, WI) volumetric feeder. Starch and wax OP were added at barrel section six using a K-tron (Pitman, NJ) gravimetric twin-screw

feeder. Extruded pellets were injection molded into ASTM type I tensile bars (16.51×1.91×0.318 cm, 6.5×0.75×0.125 inches) using a Cincinnati Milacron Act-75-B molder. Mold temperatures were 70–100 °C.

Bars (three replications) were sewn into nylon mesh bags and buried in soil approximately 6 inches deep in NCAUR on-site plots starting in July 1999. Soil temperatures were measured by inserting a thermometer to a depth of approximately 6 inches. Soil moistures were measured by weight loss after heating soil obtained at

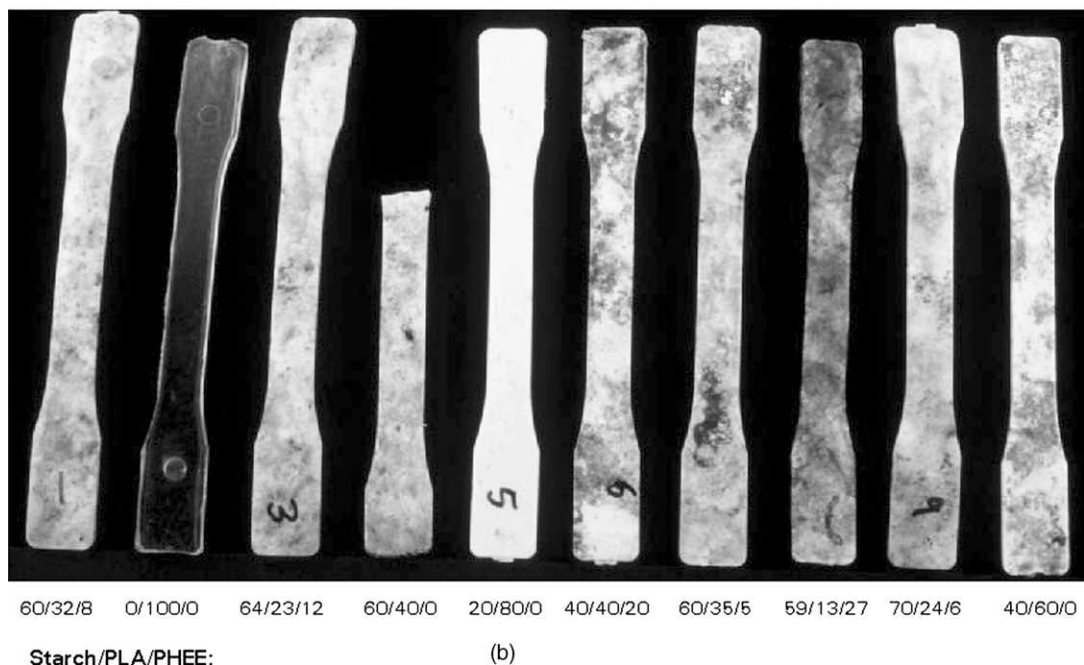
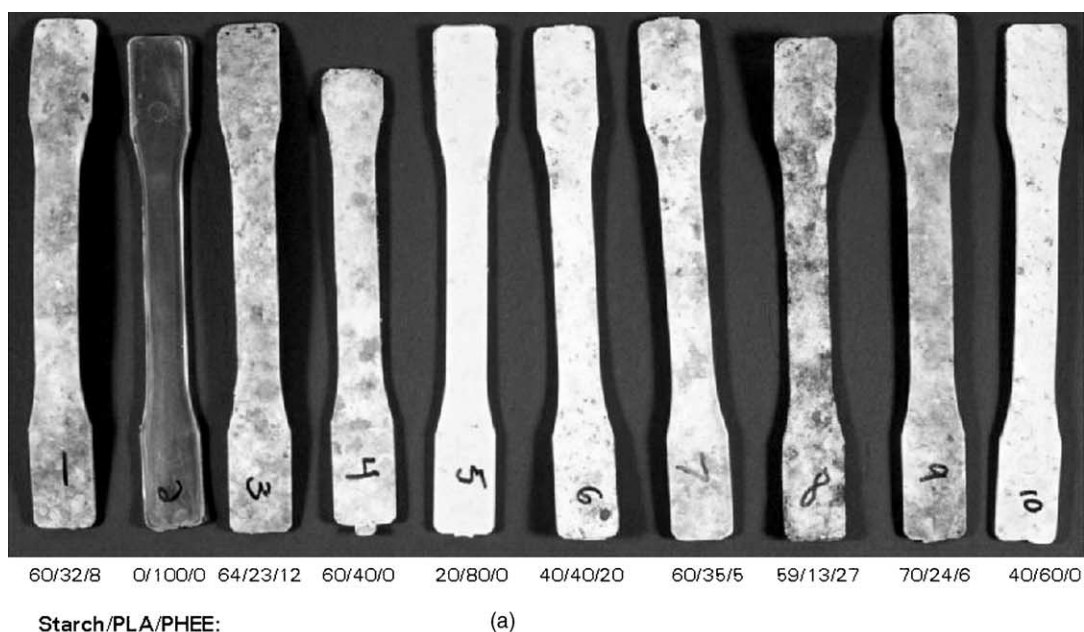


Fig. 2. (A) Photographs of starch/PLA/PHEE bars after 3 months in soil. (B) Photographs of starch/PLA/PHEE bars after 12 months in soil.

the 6 inch depth at 105 °C for 20 min. Historical data on soil temperature and moisture are shown in Fig. 1. After removal from the ground, bars were gently washed with water and equilibrated at 23 °C, 50% r.h. Bars were weighed monthly until a constant weight was obtained. Bars were subsequently tested for tensile properties using an Instron 4201 (Canton, MA) according to ASTM D638. Crosshead speed was 50 mm/min. Weight

and tensile data presented are averages of the three replicate bars. Compositions of selected bars were measured by dissolving 1 g of bar in 20 ml tetrahydrofuran (THF) in a glass stoppered flask by heating to 40–45 °C followed by occasional shaking for 1 week. The supernatant was pipetted off, the residual starch washed with an additional 5 ml of THF and the residual starch and PLA + PHEE extracts dried and weighed. About 1 mg

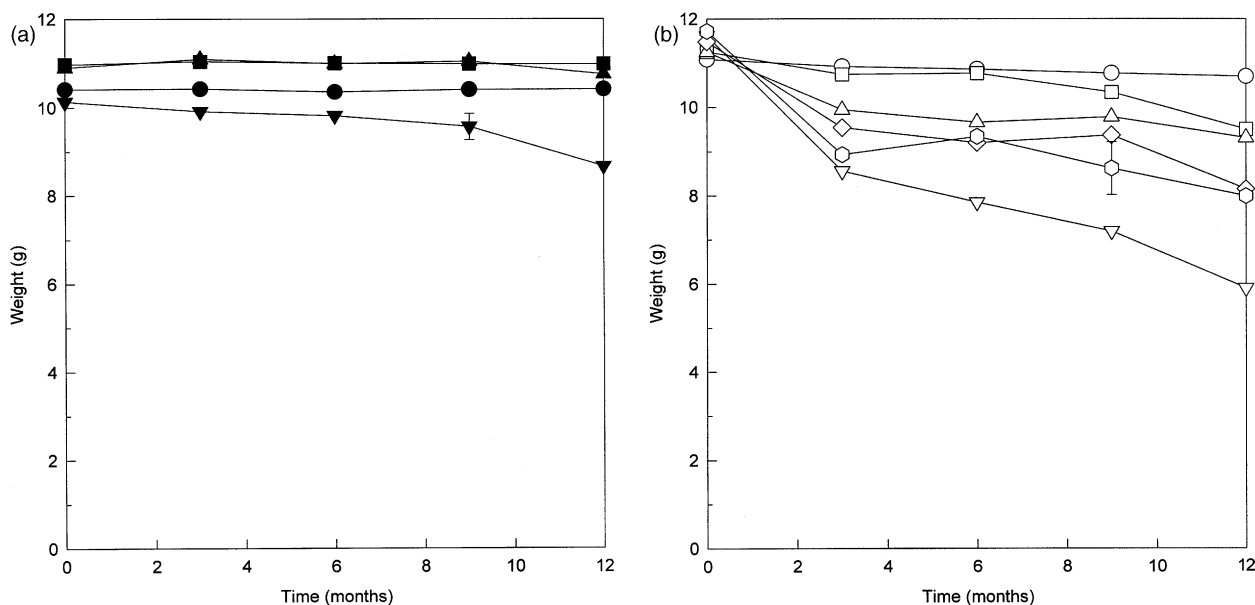


Fig. 3. (a) Effect of time of soil burial on weight of molded starch/PLA bars. Samples were: pure PLA (●); starch/PLA 20/80 (■); starch/PLA 40/60 (▲); starch/PLA 60/40 (▼). (b) Effect of time of soil burial on weight of molded starch/PLA/PHEE bars. Samples were: starch/PLA/PHEE 40/40/20 (○); 60/35/5 (□); 60/32/8 (△); 60/13/27 (▽); 65/23/12 (◇); 70/24/6 (○).

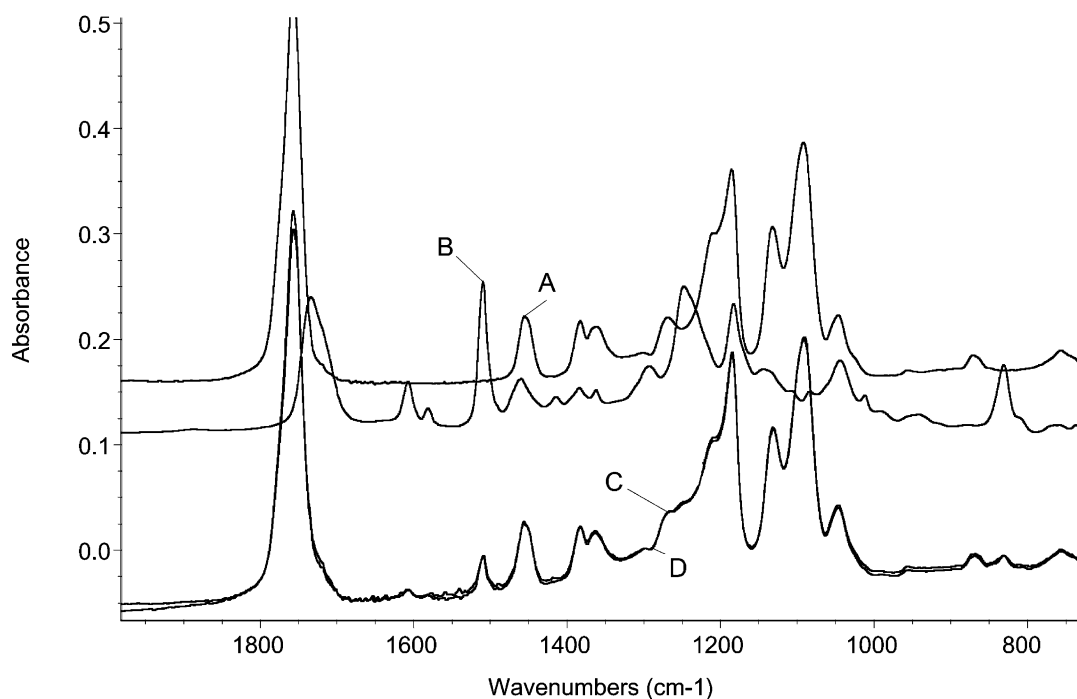


Fig. 4. FTIR spectra of pure PLA (A); pure PHEE (B); THF extract of starch/PLA/PHEE 60/32/8 (C); THF extract of starch/PLA/PHEE 60/32/8 after 12 months in soil (D).

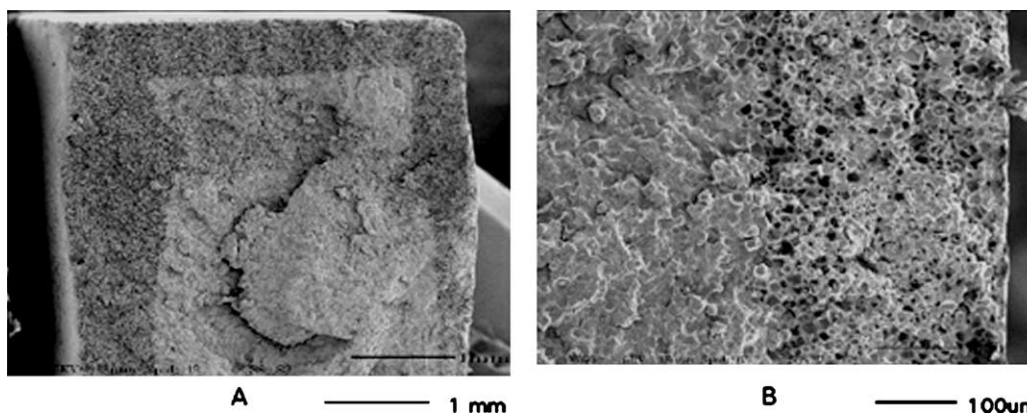


Fig. 5. Scanning electron micrographs of cross-section of starch/PLA/PHEE 60/35/5 bar after 12 months in soil. A: 25 \times , B: 250 \times .

Table 1

Loss of starch versus polymer in bars buried for 12 months as determined by extraction of PLA/PHEE with tetrahydrofuran and weighing

Treatment number	Initial composition, starch/PLA/PHEE	Loss of starch (wt.%)	Loss of PLA + PHEE (wt.%)
4	60/40/0	31	0
7	60/34/6	39	0
1	60/32/8	39	0
8	60/13/27	83	0

of extract was redissolved in THF, coated onto a ZnSe disc and FTIR spectra were obtained using a Nicolet Impact 410 spectrometer (Madison, WI).

3. Results and discussion

Fig. 2A and B show photographs of starch/PLA/PHEE bars after 3 and 12 months in soil. Fig. 3A and B show changes in bar weight with time of soil burial. The 60/40/0 bars were all shorter and lower in weight than the others because, even at maximum injection pressure, molten blends were too viscous to allow complete mold filling. Interestingly, addition of small amounts of PHEE allows complete mold filling even at higher (70%) starch levels, presumably due to reduction in melt viscosity. The pure PLA bar showed no weight change over 1 year and looked like new (no discoloration, pitting, etc.). Bars containing 20 or 40% starch also showed little weight change while those with 60% showed a slow decline. Discoloration presumably due to microbial growth began to occur at 3 months for the 60% starch sample and was more prominent at 12 months for both 40 and 60% starch. Addition of PHEE caused more rapid discoloration and weights to decline more rapidly, with rates increasing with higher starch and PHEE levels. The largest weight loss was 50% for a starch/PLA/PHEE 60/13/27 formulation.

From weights of residual starch and THF extracted PLA/PHEE, it was determined that all weight loss was due to loss of starch. Data in Table 1 indicate that losses of starch ranged from 31% for the 60/40/0 sample to 83% for the 60/13/27 sample. FTIR spectra (Fig. 4) of the THF extracts of the 60/32/8 bar at 0 and 12 months were identical, indicating that PLA/PHEE ratios were the same and thus neither PLA nor PHEE were lost preferentially after 12 month in soil. Similar FTIR results were obtained for treatments 4, 7 and 8 (treatments defined in Table 1). Molecular weight degradation may have been taking place but this was not measured.

Scanning electron micrographs (Fig. 5) of cross sections of broken, buried bars revealed that starch was lost from the surface of the bar inward with a narrow zone of partially degraded starch granules evident. Within the zone of degradation, partially degraded starch granules could be visualized, suggesting that removal of starch was due to microbial action rather than physical removal (i.e. granules popping out). Also, similar SEM micrographs (data not shown) were seen for samples which had been sectioned with a razor blade rather than broken by pulling in the Instron, indicating that starch granule loss was not due to mechanical stresses during fracture.

Tensile strengths of the bars as functions of burial time are shown in Fig. 6A and B. Zero time values represent measurements 1 month after molding at 23 °C, 50% r.h. There is little change in the tensile strength of pure PLA (65 MPa) with time. Tensile strengths of starch/PLA bars have a steep initial decline then remain fairly constant for the remainder of the burial period. This is probably due to absorption of water during soil burial with consequent weakening of starch/PLA adhesion. A constant strength with concurrent loss of starch suggests that there was little or no adhesion of starch to the polymer matrix once moistened in soil. Tensile strength decreased with increasing starch level due to relatively weak starch/PLA adhesion, as shown previously [6]. Similar decreases in tensile strength after

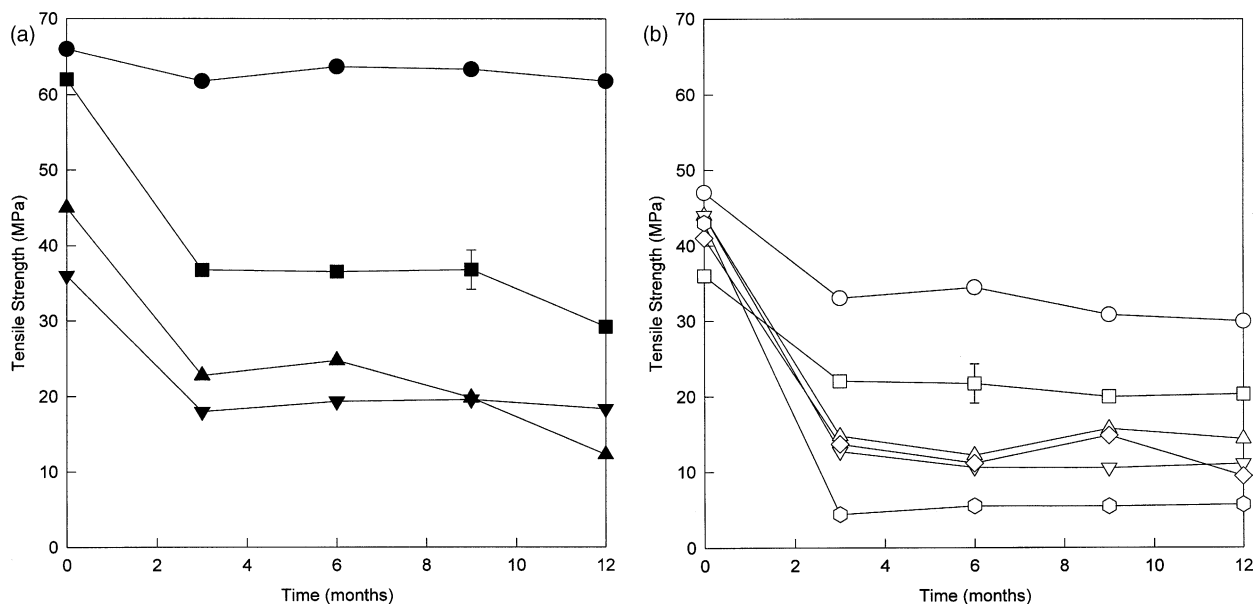


Fig. 6. (a). Effect of time of soil burial on tensile strength of molded starch/PLA bars. Samples were: pure PLA (●); starch/PLA 20/80 (■); starch/PLA 40/60 (▲); starch/PLA 60/40 (▼). (b) Effect of time of soil burial on tensile strength of molded starch/PLA/PHEE bars. Samples were: starch/PLA/PHEE 40/40/20 (○); 60/35/5 (□); 60/32/8 (△); 60/13/27 (▽); 65/23/12 (◇); 70/24/6 (○).

short burial times and then slower change for longer times were also seen for formulations containing PHEE. Slow declines in strength with time were also seen for samples equilibrated at 50% r.h. for many months (data not shown), probably due to water absorption and loss of starch/polymer adhesion. Some samples containing PHEE seemed to have higher strength after initial exposure to soil than those that did not. For example, starch/PLA/PHEE 40/40/20 had tensile strength of 32 MPa after 3 months versus 22 MPa for starch/PLA 40/60.

PLA biodegrades slowly in ambient temperature soils probably because of the slow rate of hydrolysis at low temperatures and water contents and the relative scarcity of PLA degrading organisms [11,14]. Given the relatively thick samples used here, permeation of water into the interior of the PLA bars will be relatively slow. Also, the water content of the soil was relatively low, ranging from about 15 to 25% and temperatures were cold during the winter season. Still, it is somewhat surprising that little change in PLA strength was observed over 1 year, given the propensity of PLA to hydrolyze. Even adding up to 60% starch to PLA did not accelerate weight loss of PLA and the starch itself remained mostly inaccessible to microbial action, perhaps coated by the PLA. The starch in samples containing PHEE was much more accessible to biodegradation. Perhaps the softer PHEE ($T_g = 37^\circ\text{C}$ dry, 20°C wet) [27] could be more easily penetrated by microbes. Even with this porous network which should provide easy entry for water, there was no detectable loss of PLA and little decline in strength (after initial decline). Presumably molecular weights decreased as was previously found

for starch/PLA composites buried in soil [24] but this was not measured.

Based on the earlier results, it appears that the rather thick starch/PLA/PHEE composites used here would require many years to biodegrade in a relatively cool and dry soil environment. Thus soil burial would probably not be an acceptable way to dispose of such materials either intentionally or by careless "littering" of single-use plastic articles. Thin PLA composite films would certainly degrade much faster due to more rapid diffusion of water and greater specific surface area for microbial attack. However, even thin films of PLA may require years to degrade depending on the particular environment [21–23,28] and problems previously seen with use of "degradable" polyethylene films, such as pieces of partially degraded plastic bags or mulch blowing around and strangulation or intestinal blockage in animals are potential problems for PLA as well. It may become important to educate consumers that, although PLA articles would be compostable, they should not be discarded randomly in the environment. There may be ways to accelerate the biodegradation of PLA in natural environments such as copolymerization, blending in acidic compounds or perhaps proteins which might induce the production of proteases by microorganisms which have been found to degrade PLA. Preferred methods of disposal would be composting and/or recycling.

In summary, injection molded polylactic acid (PLA) bars are slow to degrade in soil (years). Addition of granular starch (up to 60% by weight) to PLA does not significantly accelerate the degradation (weight loss) of

PLA and even most of the starch remains intact after 1 year in soil. Addition of PHEE to starch/PLA increases the rate of degradation though all weight loss was due to starch alone. It would be expected that the PLA in such a porous bar would, however, eventually biodegrade and fragment more quickly due to increased surface area and accessibility to microbes, especially for thinner specimens. Addition of PHEE also allowed bars with higher starch content (up to 70%) to be molded and may give higher strengths under certain (moist) conditions.

Acknowledgements

The authors thank E. Krietemeyer, B. Nichols and B. Jasberg for help with processing and soil burial and Dr. A. Thompson for scanning electron microscopy. This work was performed under Cooperative Research and Development Agreement 58-3K95-0-814 between the Agricultural Research Service and the Biotechnology Research and Development Corporation.

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